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TECHNICAL MEMORANDUM

March 16, 2014

To: Jeffrey Rosen, Corona Environmental Consulting

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Subject: Expert Panel Estimates of the Odor Threshold Concentration, Odor Recognition Concentration and Odor Objection Concentration for Crude 4-methylcyclohexanemethanol in Water

EXECUTIVE SUMMARY

A spill of “Crude” 4-methylcyclohexanemethanol (MCHM) into the Elk River in West Virginia resulted in odor complaints by residents in their tap water downstream of the spill—predominantly a licorice odor. A team of experts was hired to understand the odor characteristics of the spilled chemical. The expert team developed a methodology based on ASTM Method E679¹ to estimate the Odor Threshold Concentration (OTC), Odor Recognition Concentration (ORC) and Odor Objection Concentration (OOC) for Crude MCHM in water during a single panel session.

A number of qualifiers must be attached to the findings of this report:

1. Only nine panelists were used in the study and two-thirds of the panelists were women as opposed to the 50:50 desired gender distribution
2. Most of the panelists were young and not representative of the ages in Charleston, WV; younger people generally have lower individual thresholds than older people
3. All nine of the panelists were experts who have been assessing taste and odor problems in drinking water
4. Everyone on the panel knew that we were working with Crude MCHM from the spill in West Virginia; many of them had smelled Crude MCHM before the panel study as part of the method development at UCLA
5. Arrowhead spring water was used as the matrix water which has different chemical characteristics compared to treated water from the Elk River
6. Chlorine, which can mask other odors, was not in the water samples assessed by the panel

Table ES-1 summarizes the estimated OTC, ORC and OOC concentrations that were determined by the Expert Panel. The estimated OTC is in the realm of parts per trillion,

an extraordinarily low concentration. The ability of the expert human nose to detect this compound is far greater than any analytical method available today.

Table ES-1. Summary of Expert Panel Odor Threshold Estimates

Odor Thresholds	Geometric Mean, ppb	Factor: Greater than OTC
Odor Threshold Concentration (OTC)	less than 0.15	---
Odor Recognition Concentration (ORC)	2.2	15
Odor Objection Concentration (OOC) Based on Degree of Liking	4.0	27
Odor Objection Concentration (OOC) Based on Objection/Complaint	4.0	27

The estimated thresholds determined in the Expert Panel study support consumer observations in Charleston, WV that people recognized and objected to the licorice odor caused by Crude MCHM in their drinking water even though the analytical reports were showing non-detect at a minimum reporting level of 10 ppb.

Recommendations for future work have been made including the convening of a larger panel to determine estimates of OTC, ORC and OOC for Crude MCHM using untrained consumers.

INTRODUCTION

On January 9, 2014, approximately 10,000 gallons of “Crude” 4-methylcyclohexane-methanol (MCHM) spilled into the Elk River from the property of Freedom Industries a short distance above the drinking water intake of the West Virginia American (WVA) water treatment plant. Shortly after the spill began, consumers located in the area served by WVA (Charleston, WV and environs) began complaining of a licorice odor in their drinking water. On February 9, I was hired as part of an expert team to help the state of West Virginia understand the odor characteristics of the spilled chemical and the reactions of the customers served by WVA.

It was urgent that the odor characteristics of the chemical be understood in a scientific context in a short period of time. Therefore, an Expert Panel study was planned which could give some answers in a matter of a few weeks.

The objectives of the work described in this technical memorandum were to:

1. Develop a methodology to estimate the Odor Threshold Concentration (OTC), Odor Recognition Concentration (ORC) and Odor Objection Concentration (OOC) for the licorice-smelling substance in water.

2. Work with an analytical laboratory to develop a spiking method to prepare samples of the licorice-smelling substance in a reference water that could be presented to a panel.
3. Convene a panel of experts to participate in a study using the methodology developed to estimate concentrations of detection, recognition and objection/complaint for the licorice-smelling substance in water.
4. Understand how the Expert Panel results could explain consumer observations in Charleston, WV where people smelled a licorice odor in their drinking water immediately after the spill and for many weeks following the spill even after repeated system flushing.
5. Make recommendations for additional work to supplement and confirm the Expert Panel findings.

DEFINITIONS OF DETECTION (THRESHOLD), RECOGNITION AND OBJECTION CONCENTRATIONS

Understanding how consumers react to off-odors in their drinking water is a complex problem that presents a unique set of challenges. To understand this phenomenon, it is important to appreciate the distinction between detectable odors and the concepts of recognizable and objectionable odors. Peer-reviewed scientific literature has recognized the concepts of detection, recognition and objection of odors in drinking water and other substances.^{2, 3, 4} Table 1 organizes the concentrations of odorants in drinking water into aesthetic response levels.

Table 1. Odor Response Levels for Concentrations of Chemicals in Water

Odor Response	Description	Aesthetic Response Levels
Detection (Threshold)	Chemical concentration usually determined in a laboratory setting where approximately 50% (calculated by geometric mean) of panelists can just detect the odor of a chemical	Odor threshold concentration—OTC
Recognition	Concentration of a chemical where approximately 50% (calculated by geometric mean) of panelists can correctly recognize and describe the odor characteristics of the chemical	Odor recognition concentration—ORC
Objection/Complaint	Chemical concentration determined either in a laboratory or field setting that causes consumers to object to their water supply and to call and complain	Odor objection concentration—OOC

The same principles in Table 1 apply to the sense of taste. For example, the taste thresholds for sodium chloride and calcium chloride are in the range of 200 to 300 mg/L.⁵ At or above the taste threshold, panelists can describe the “salty” taste resulting in recognition. As the sodium chloride concentration is increased further, the salty taste becomes objectionable.

Concentrations of minerals (including sodium chloride) that are objectionable to consumers in actual drinking water distribution systems have been described by detailed surveys of households. Bruvold and Daniels found that total dissolved solids (TDS) concentrations above 450 mg/L caused a significant number of consumers to reject their water supply and to seek alternatives. This concentration is just below the Secondary Maximum Contaminant Level for TDS and is equivalent to the taste objection concentration for TDS.⁶

PANEL METHODOLOGY

Panelists were recruited for this study using the following criteria:

- Expert panelists trained in the Flavor Profile Analysis (FPA) method^{7, 8}
- Between the ages of 18 and 65
- Balance of women and men (approximately 50:50)
- Pregnant women could not participate
- Non-smokers only
- Anyone with a history of severe asthma or sinus problems was excluded
- Anyone currently suffering from a cold, the flu or any upper-respiratory disease at the time of testing was excluded
- No eating or drinking anything but water for one hour prior to testing

The Expert Panel was composed of nine individuals—three from the consulting engineering firm of Hazen and Sawyer (H&S) and six from a research group at the Environmental Health Science Department of the University of California, Los Angeles (UCLA). The H&S experts conduct assessments of water samples on a routine basis for their firm. All six of the UCLA panelists had been trained in the FPA method, and they had participated in research studies on taste and odor for several months to several years prior to this study. The panel sessions were held on Friday, February 21 and Monday, February 24 at H&S and UCLA, respectively.

The gender split for the Expert Panel was 67:33, female to male. Figure 1 shows the distribution of ages of the panel. Because students made up most of the panel, it is not surprising that the 18 to 33 age category contains 56 percent of the panelists.

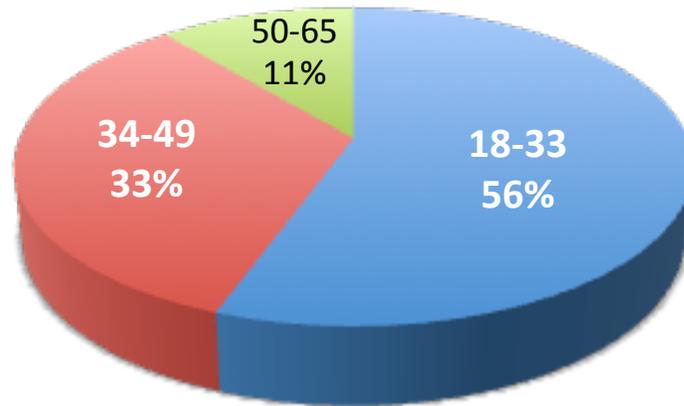


Figure 1. Age Distribution of Expert Panel Study

The H&S panel was held in a business office setting where cups of water for testing were delivered to the panelists at their desks. There were no fugitive odors in the office that interfered with odor detection. The UCLA panel was held in a special odor panel room in the School of Public Health maintained by Dr. I. H. Suffet. Each UCLA panelist conducted his/her assessment of the samples in specially constructed booths that ensured privacy and independent determination—see Figure 2.



Figure 2. Taste and Odor Testing Room at UCLA

Source of Crude MCHM

A 100 mL sample of the same Crude MCHM that spilled into the Elk River was collected by SGT Charles Cook of the West Virginia Army National Guard on February 12 and shipped overnight to my Santa Monica home. I transferred the sample to a fume hood at the UCLA laboratory the next day. The sample came from Tank SV35927LM at the Poca Blending Facility. The contents of that tank were transferred from the leaking tank on the property of Freedom Industries sometime after the leak was discovered.

Odor Assessment of Chemical to Spike into Water for Threshold Determinations

I assessed the odor characteristics of Crude MCHM and a pure standard of MCHM obtained from the chemical supply company TCI America. The Crude MCHM had a licorice odor that was penetrating, irritating and sharp. The pure MCHM had a definite licorice odor, but it was milder than the Crude. The MSDS form for Crude MCHM that accompanied the sample of the spilled tank contents showed that pure MCHM was the major component but other minor constituents were present. Figure 3 shows a chromatogram of Crude MCHM in methanol that was run on the Varian 450GC/220MS instrument in the UCLA laboratory showing MCHM and some of the minor constituents. We know from smelling a pure standard that dimethyl 1,4-cyclohexanedicarboxylate does have a licorice odor that is about the same characteristic and intensity as pure MCHM.

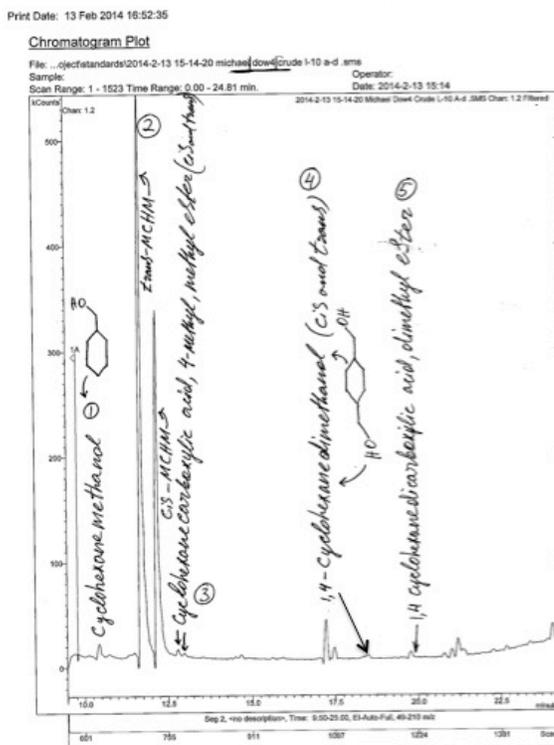


Figure 3. Chromatogram of Crude MCHM Showing Minor Components

Given the differences in the odor characteristics of the pure and Crude MCHM, it seemed plausible that one or more of the minor constituents of the Crude MCHM could be adding to the more obnoxious characteristics of the odor. Therefore, Crude MCHM was chosen as the chemical to spike into the water that would be presented for odor assessment to the panelists.

I also assessed the odor associated with the pure chemical propylene glycol phenyl ether (PPH), which was listed as one of the minor components of Crude MCHM. Pure PPH does not have a licorice odor of any kind. Instead, its odor can be characterized as mild, ether-like. No further odor work with PPH has been conducted.

Selection of Matrix Water

We could not use treated water from the Elk River as the water for our tests because of the obvious problem that we did not know if the licorice odor was absent from the source. Also, the goal was to conduct threshold studies on water without chlorine. Chlorine interference with odor thresholds is well established and the impact of chlorine on the odor characteristics of MCHM in water is the subject of future research.

Based on several decades of experience in the field of taste and odor in water, I determined that we needed spring water with no off-flavors for the panel matrix water.^{9, 10, 11} Arrowhead spring water was chosen because it is widely available in Southern California where the panel studies would take place. The odor quality of Arrowhead spring water is consistent, and in my experience, I have never detected off-odors in that product.

Twenty-seven liters of Arrowhead spring water were purchased in several stores in Southern California in 3-L containers and used as the blank water in the Expert Panel threshold tests.

Preparation of Spiked Samples and Determination of Crude MCHM Concentrations

Eurofins Laboratory in Lancaster, PA was chosen as the site to prepare the spiked samples of Crude MCHM, because it is the laboratory that is running the MCHM analytical method with a method detection level (MDL) of 0.5 ppb and a method reporting level (MRL) of 1.0 ppb. To the best of my knowledge, these concentrations are the lowest currently being determined by any laboratory in the U.S. Concentrations in the spiked samples were based on spiking 100% crude MCHM. The laboratory measured total peak area for the *trans* and *cis* isomers of MCHM and used this marker to determine the recovery of spiked concentrations in water.

The following is a summary of the Eurofins MCHM analytical method: A water sample is serially extracted with methylene chloride. The resulting extract is reduced in volume and an aliquot injected into a gas chromatograph equipped with a mass spectrometer detector (GC/MS). The GC/MS analytical system is tuned and calibrated following the

principles outlined in SW-846, Method 8270D. This includes tuning the system to decafluorotriphenylphosphine (DFTPP) relative mass abundance criteria and calibration using a minimum of five calibration points from 1 ppb to 60 ppb. The analytical system is tuned and the calibration responses are checked every 12 hours.

As a routine part of the extraction procedure, a method blank, a laboratory control sample (LCS) and an MRL LCS are extracted along with every group of field samples that are analyzed. A method blank that is free of target compounds and an LCS and MRL LCS with acceptable recoveries of the target compounds is required for an extraction batch to be considered acceptable.

Unfortunately, Arrowhead spring water is not available in Lancaster, PA. Therefore, several gallons of Arrowhead spring water were purchased in Southern California and shipped to the Lancaster facility. The matrix water was spiked with Crude MCHM at eight levels with concentrations ranging from 0.16 to 100 ppb. Subsamples of the spiked water were analyzed immediately using the Eurofins analytical method. Two liters each of the eight levels of spiked samples were shipped overnight to the UCLA laboratory. On Wednesday, February 24 after the Expert Panels were complete, Eurofins analyzed another subsample of the spiked matrix water.

Reference Odor Descriptors from Each Panelist

Prior to conducting any of the Expert Panels, individual panelists were taken aside and told that they would be sniffing water that may have odors that were similar to a reference odor that I would be presenting to them. They were also told that they might not recognize any odors in the water samples that were anything like the reference odor. They were asked to carefully sniff a diluted sample of Crude MCHM and explain in their own words how they would describe the odor. Their descriptions of the reference odor were recorded on a form.

Panelist Instructions

After the reference odors were recorded, the panel moderator read a script to the assembled panels which described the methods and procedures that they would use and the way that they would record their observations and opinions, see Appendix A. While the panel was underway, the moderator walked around the panel testing area asking for any questions or clarifications and observing whether or not the panelists were following instructions. In a few cases, the moderator repeated instructions to individual panelists.

Odor Threshold (Detection) Concentration Method

The well-known methodology referred to as ASTM E679-04 (2011) was used to estimate the OTC for Crude MCHM.¹² The same method was used in 1998 to determine the OTC for methyl *tert*-butyl ether (the gasoline additive MTBE) in water using a consumer panel.¹³ For the UCLA study, three ounces of spiked and blank water were placed in nine-ounce odor-free plastic cups and covered with watch glasses, see Figure 4. Each

panelist was presented with three cups at a time. One of the cups contained the spiked sample and the other two cups contained blank water. The panelists were asked to pick up each cup and watch glass, gently swirl the water in the cup, lift the watch glass and sniff the headspace above the water replacing the watch glass when they were finished. The panelists were instructed to then choose the odor in the cup that was different from the other two.



Figure 4. Sample Presentation to Panelists

Even if the panelists could not tell the difference between the three cups, they had to choose one of them as different. They could re-sniff the cups if they wished. The panelists received the lowest concentration of spiked water first. Subsequent groups of three cups contained one spiked sample with increasing concentrations of Crude MCHM to a maximum of 100 ppb. They recorded their observations by circling the code of the different cup on the score sheet. Appendix B shows the score sheet used in the Expert Panels.

Random numbers were used to code all of the cups. The location of the different cup containing the spiked sample was roughly split between the left, middle and right cup. This presentation and scoring methodology is generally referred to as a forced-choice triangle, ascending (concentration) series. Temperatures of the UCLA spiked and blank water in the cups ranged from 20 to 22 degrees Celsius.

The presentation method for the H&S panel was the same except five-ounce odor-free plastic cups were used and about two ounces of water was placed in each cup. Temperatures of the H&S spiked and blank water in the cups were 18 to 22 degrees Celsius.

Odor Recognition Concentration Threshold Method

Next, panelists were asked to record on the score sheet what they thought the water in the different cup smelled like. They were told that they should use any terminology that described the characteristic of the odor in the different cup, or they could use the terms for the reference odor if they recognized it. If the water smelled like nothing (had no odor), the panelists could write “nothing.”

The ASTM E679 technique recognizes the determination of an ORC as part of its methodology. “...*recognition threshold*—the lowest concentration of a substance in a medium relating to the lowest physical intensity at which a stimulus is recognized as determined by the best-estimate criterion.”¹⁴ (italics in original)

Methods for Determining Odor Objection Concentrations

There is no generally accepted methodology for determining a level of objection to the odor of an organic compound in water. In this research, two methods were used to answer the question: When do we know that panelists object to something in the water they are testing?

The first approach used the widely accepted methodology¹⁵ of presenting a stimulus to a panelist and asking how much the panelist liked or disliked the stimulus using a hedonic scale for the panelist to score his/her judgments. The nine-point hedonic scale used for this work was taken from *Standard Methods*.¹⁶

The second approach is based on my experience determining when the concentration of a substance in water has reached the objection level in a water utility distribution system. When a significant number of consumers object to an odor in their drinking water, some of them will pick up the telephone and call to complain. Not all who object will complain, but it will be clear to water utility management when the telephone calls start rolling in that they have a problem.

From my experiences at the Metropolitan Water District of Southern California with earthy-musty odor problems, there is a clear “tipping point.” Earthy-musty odors are generally caused by blue-green algae producing two compounds: geosmin and 2-methylisoborneol (MIB). Published OTCs for these compounds vary but they are generally around 4 parts per trillion (ppt). When 10 ppt of either compound (or both adding up to 10 ppt) is being served to consumers, some of them will definitely call and complain. For both of these compounds, 10 ppt is the Odor Objection Concentration. A number of water utilities have set 10 ppt as their treatment goal to avoid complaints. Other utilities that desire a more stringent goal have set 5 ppt for both geosmin and MIB.

Odor Objection Concentration Threshold Method—Degree of Liking

The panelists were asked to rate how much they liked or disliked the odor of the water in the different cup. Appendix C shows the degree of liking scale that the panelists used to assess how much they liked or disliked the odor. They recorded their rating from the scale on the score sheet in the “Degree of Liking” column.

Odor Objection Concentration Threshold Method—Objection/Complaint

Finally, it was suggested to the panelists that they might find some of the odors in the different cups objectionable. If the odor was objectionable and the panelist would complain to her/his water utility or bottled water company, they were instructed to answer, “Yes” in the “Object/Complain?” column.

Collection and Organization of Score Sheets

After the eighth sample set was completed, the moderator collected the score sheets and checked them to make sure that the panelists had followed the instructions properly, and that all of the descriptions and scores were filled in. The data from the panels were entered into an Excel spreadsheet and the best estimate thresholds for individuals and the panel as a whole were determined using the geometric mean calculation specified in ASTM E679.

RESULTS AND DISCUSSION

Analytical Results of Spiked Samples

Table 2 shows the concentrations of Crude MCHM recovered and the percent recoveries for samples analyzed before and after the Expert Panels were conducted. The data show good recoveries for spiked concentrations above the method MRL of 1 ppb ranging from 90 to 116 percent (within the acceptable range of 80 to 120%). As expected, most of the recoveries at and below the MRL are outside the generally acceptable range. None of these results indicate that the spiked concentrations of Crude MCHM degraded over the holding period. The data on Table 2 show the variability of the MCHM analysis and spiking processes, especially at concentrations at and below 1 ppb.

Table 2. Spiked Recoveries of Crude MCHM Determined by Eurofins Laboratory

Spiked Crude MCHM, ppb	Crude MCHM Recovered, ppb		Percent Crude MCHM Recovered	
	Pre-Panel Analysis	Post-Panel Analysis	Pre-Panel Analysis	Post-Panel Analysis
0.16	0.12	0.073	74%	44%
0.41	0.33	0.27	81%	65%
1.0	0.91	0.77	89%	76%
2.6	2.6	2.3	103%	90%
6.4	7.0	6.6	109%	103%
16	18	18	111%	111%
40	44	46	110%	116%
100	99	104	99%	104%

Note: Pre-Panel analyses were conducted on 2/18/14; Post-Panel analyses on 2/24/14; rounded to 2 significant figures and zero decimal places for the percent recoveries

Odor Threshold Concentration

Table 3 shows the results of the OTC determination for the nine panelists. The estimate of the individual odor thresholds is calculated as the geometric mean of the concentration where the last incorrect cup was chosen and the next higher concentration where the correct cup was chosen from there upward. An incorrect cup choice is recorded on the table as a “0” and a correct choice as a “+”. Thus, the estimate of the OTC for Panelist 09 is the geometric mean of 1.0 and 2.6 or 1.6 ppb.

For those sensitive panelists who correctly chose the different cup at all eight concentrations, the estimate of their individual OTC is the geometric mean of the lowest concentration presented (0.16 ppb) and the concentration at the next lower step, which in this case would be 2.5 times lower or 0.064 ppb. Thus, the estimate of the OTC for Panelist 02 is the geometric mean of 0.16 and 0.064 or 0.10 ppb.

Table 3. Expert Panel Results for Odor Threshold Concentration

Panelists	Date Study Conducted	Concentrations of Crude MCHM Presented to Panelists, ppb								Best Estimate Threshold, ppb
		0.16	0.41	1.0	2.6	6.4	16	40	100	Value
02	2/21/14	+	+	+	+	+	+	+	+	0.10
03	2/21/14	+	+	+	+	+	+	+	+	0.10
04	2/21/14	+	+	+	+	+	+	+	+	0.10
07	2/24/14	+	+	+	+	+	+	+	+	0.10
08	2/24/14	+	+	+	+	+	+	+	+	0.10
09	2/24/14	+	+	0	+	+	+	+	+	1.6
10	2/24/14	0	+	+	+	+	+	+	+	0.26
11	2/24/14	+	+	+	+	+	+	+	+	0.10
12	2/24/14	+	+	+	+	+	+	+	+	0.10

Note: “0” indicates that the panelist selected the wrong sample of the set of three; “+” indicates that the panelist selected the correct sample; the individual OTC is the geometric mean of the two concentrations where there is a change from “0” to consistent answers of “+” which is noted by gray-shaded cells. The actual OTC for these panelists is less than 0.15 ppb

Geometric Mean, ppb = < 0.15

The calculated estimate of the OTC for Crude MCHM determined by these panelists is the geometric mean of the nine individual geometric means, or 0.15 ppb. However, because seven of the nine panelists correctly identified the different cups at all eight concentrations, the true OTC for this group of sensitive individuals is most likely below 0.15 ppb. Therefore, for this study, the OTC for Crude MCHM in water will be reported as less than 0.15 ppb.

Based on the findings from this study, the lowest concentration presented to the Consumer Panel should be less than the lowest concentration presented to the Expert Panel, 0.16 ppb. While the expert panelists used in this study can usually detect OTC values lower than consumers, lower concentrations must be presented to the consumer panelists to ensure that most of the correct responses are captured in the concentration range used.

Odor Recognition Concentration

Table 4 indicates that all expert panel members specified the reference odor in their odor descriptors. An ORC was only recorded for concentrations at or above the individual panelist's OTC. The best estimate of the individual panelist ORC is the geometric mean of the two concentrations where there is a change from "other" descriptors to the reference odor descriptor, which is noted with gray-shaded cells. For panelist 03 for example, the descriptor of "lemony" at 0.41 ppb changed to "anise" at 1.0 ppb. The panelist's individual ORC is the geometric mean of those two concentrations, 0.64 ppb.

Table 4. Expert Panel Results for Odor Recognition Concentration

Panelists	Date Study Conducted	Concentrations of Crude MCHM Presented to Panelists, ppb								Reference Odor	Best Estimate Threshold, ppb
		0.16	0.41	1.0	2.6	6.4	16	40	100		Value
02	2/21/14	licorice	licorice, sweet	licorice, syrupy sweet	licorice, solvent, syrupy sweet	syrupy sweet, pineapple juice	syrupy sweet, pineapple juice	syrupy sweet, ripe fruit	syrupy sweet, ripe fruit	Licorice, sweet, woody	0.10
03	2/21/14		lemony	anise	anise	anise, lemony	anise, cough syrup	lemony, bile, anise	lemony, bile, anise	anise, sweet, vanilla	0.64
04	2/21/14						paints, gasoline exhaust	sweet chemical	sweet chemical	flowery, sweet, hand wipes chemical	25
07	2/24/14	sweet, grassy (fades)	sweet, faint licorice, candy	faint sweet	faint sweet, licorice	sweet licorice	faint sweet licorice	faint sweet licorice	sweet licorice	sweet, licorice, candy	0.26
08	2/24/14		sweet	sweet, licorice	sweet, licorice	sweet, licorice	sweet, licorice	sweet, licorice	sweet, licorice	sweet, licorice	0.64
09	2/24/14				fruity, sweet	licorice, sweet	licorice, sweet	pine, licorice, sweet	licorice, sweet	fruity, pine, licorice	4.1
10	2/24/14					strong solvent, sweet	licorice, sweet	licorice, sweet	licorice, sweet	licorice, pine	10
11	2/24/14					sweet, refreshing	sweet, licorice	sweet, licorice	sweet, licorice	licorice	10
12	2/24/14					glue, rubbery	glue, rubbery, licorice	glue, rubbery, licorice	sweet, licorice, glue	sweet, licorice	10

Notes: The ORC was only recorded for concentrations at or above the OTC; the individual ORC is the geometric mean of the two concentrations where there is a change from other descriptors to the reference odor descriptor which is noted by gray-shaded cells. Descriptors are not shown below individual ORC thresholds.

Geometric Mean, ppb = 2.2

One panelist was able to characterize the odor of the different cup as their reference odor of “licorice” at the lowest concentration presented, 0.16 ppb. The estimate of their individual ORC is the geometric mean of the lowest concentration presented (0.16 ppb) and the concentration at the next lowest step, which in this case would be 2.5 times lower or 0.064 ppb. Thus, the estimate of the ORC for Panelist 02 is the geometric mean of 0.16 and 0.064 or 0.10 ppb.

Below the individual ORCs, many of the panelists noted that the correctly chosen different cup smelled “sweet.” This was not sufficient to provoke a match with the reference odor descriptor for expert panelists. It is not unusual for organic chemicals to elicit a sweet odor description from expert panelists. In my own experience, the odor of MTBE has a sweet odor characteristic at concentrations below the level where the reference odor (sweet solvent) is recognized.

The calculated estimate of the ORC for Crude MCHM determined by these panelists is the geometric mean of the nine individual geometric means, or 2.2 ppb. Most of the individual ORC concentrations were within the range of concentrations presented, 0.16 to 100 ppb. The ASTM method states: “If the concentration range has been correctly selected, all panelists should judge correctly within the range of concentration steps provided.”

Odor Objection Concentration

As noted in the Panel Methodology section of this memorandum, two methods were used to estimate the OOC for Crude MCHM. Table 5 shows the results for the OOC determination based on the degree of liking scale. The OOC was only recorded for concentrations at or above the individual panelist’s OTC. The best estimate of the panelist’s individual OOC is the geometric mean of the two concentrations where there is a jump in the degree of liking score to 6 or above and the score remains at 6 or above thereafter, which is noted by gray-shaded cells on the table.

Table 5. Expert Panel Results for Odor Objection Concentration—Degree of Liking

Panelists	Date Study Conducted	Concentrations of Crude MCHM Presented to Panelists, ppb								Best Estimate Threshold, ppb
		0.16	0.41	1.0	2.6	6.4	16	40	100	Value
02	2/21/14	3	7	4	8	9	9	9	9	1.6
03	2/21/14	4	3	1	6	7	8	7	6	1.6
04	2/21/14	6	6	6	6	6	6	6	6	0.10
07	2/24/14	2	3	1	1	4	3	4	4	160
08	2/24/14	3	3	4	5	6	7	7	8	4.1
09	2/24/14	3	4	2	4	6	6	5	4	160
10	2/24/14	5	5	4	5	7	8	8	8	4.1
11	2/24/14	2	1	2	4	6	7	7	7	4.1
12	2/24/14	5	5	6	6	7	8	8	8	0.64

Note: The OOC was only recorded for concentrations at or above the OTC; the individual OOC is the geometric mean of the two concentrations where there is a jump in the degree of liking to a score of 6 or above which is noted by gray-shaded cells.

Geometric Mean, ppb = 4.0

The same method described above for OTC and ORC was used to calculate the individual OOC level when the panelist scored the lowest concentration of Crude MCHM as a degree of liking of 6 (panelist 04). For the panelists that did not score a 6 even at 100 ppb, the individual OOC was calculated as the geometric mean of 100 ppb and the next highest step, which in this case would be 2.5 times higher or 250 ppb. Therefore, the estimate of the OOC for panelist 07 is the geometric mean of 100 and 250 or 160 ppb.

The calculated estimate of the OOC for Crude MCHM using the degree of liking scale determined by these panelists is the geometric mean of the nine individual geometric means, or 4.0 ppb. Most of the individual OOC concentrations were within the range of 0.16 to 100 ppb.

Table 6 shows the results for the OOC determination based on objection/complaint. The OOC was only recorded for concentrations at or above the individual panelist’s OTC. The best estimate of the panelist’s individual OOC is the geometric mean of the two concentrations where there is a change to a consistent answer of “Yes” to the question: Would you object/complain about the odor in the different cup? The gray-shaded cells on the table note the two concentrations used to calculate the individual geometric means.

Table 6. Expert Panel Results for Odor Objection Concentration—Objection/Complaint

Panelists	Date Study Conducted	Concentrations of Crude MCHM Presented to Panelists, ppb								Best Estimate Threshold, ppb
		0.16	0.41	1.0	2.6	6.4	16	40	100	Value
02	2/21/14	N	Y	N	Y	Y	Y	Y	Y	1.6
03	2/21/14	N	N	N	Y	Y	Y	Y	Y	1.6
04	2/21/14	Y	Y	Y	Y	Y	Y	Y	Y	0.10
07	2/24/14	N	N	N	N	N	N	N	N	160
08	2/24/14	N	N	N	N	N	Y	Y	Y	10
09	2/24/14	N	N	N	N	Y	Y	Y	N	160
10	2/24/14	Y	Y	N	Y	Y	Y	Y	Y	1.6
11	2/24/14	N	N	N	N	Y	Y	Y	Y	4.1
12	2/24/14	N	N	Y	Y	Y	Y	Y	Y	0.64

Note: The OOC was only recorded for concentrations at or above the OTC; the individual OOC is the geometric mean of the two concentrations where there is a change to a consistent answer of Yes to the question: Would you object/complain about the odor in the different cup? Noted by gray-shaded cells.

Geometric Mean, ppb = 4.0

The same methods described above for OTC, ORC and OOC (Liking) was used to calculate the individual OOC levels when the panelist scored the lowest concentration of Crude MCHM as a “Yes” or the highest concentration as a “No.”

The calculated estimate of the OOC for Crude MCHM using the objection/complaint criterion determined by these panelists is the geometric mean of the nine individual geometric means, or 4.0 ppb. Once again, most of the individual OOC concentrations were within the range of concentrations presented, 0.16 to 100 ppb.

Limitations of the Methodology and Results

As with all research, there are limitations associated with this work that must be understood so that errors will not be made extrapolating the results to other applications.

- Only nine panelists were used in the study and two-thirds of the panelists were women as opposed to the 50:50 desired gender distribution
- Most of the panelists were young and not representative of the ages in Charleston, WV; younger people generally have lower individual thresholds than older people
- All nine of the panelists were experts who have been assessing taste and odor problems in drinking water
- Everyone on the panel knew that we were working with Crude MCHM from the spill in West Virginia; many of them had smelled Crude MCHM before the panel study as part of the method development at UCLA
- Arrowhead spring water was used as the matrix water which has different chemical characteristics compared to treated water from the Elk River
- Chlorine, which can mask other odors, was not in the water samples assessed by the panel

Applicability of Expert Panel Results to Understanding how Consumers Respond to Crude MCHM in Drinking Water

Table 7 summarizes the estimated OTC, ORC and OOC concentrations that were determined by the Expert Panel. Comparing the estimated OTC for Crude MCHM with thousands of others for a variety of organic compounds shows that Crude MCHM has an extremely low OTC.¹⁷ As stated previously, the estimated OTC for Crude MCHM is likely less than 0.15 ppb. That means that the OTC is in the realm of parts per trillion, an extraordinarily low concentration. The ability of the expert human nose to detect this compound is far greater than any analytical method available today.

Table 7. Summary of Expert Panel Odor Threshold Estimates

Odor Thresholds	Geometric Mean, ppb	Factor: Greater than OTC
Odor Threshold Concentration (OTC)	less than 0.15	---
Odor Recognition Concentration (ORC)	2.2	15
Odor Objection Concentration (OOC) Based on Degree of Liking	4.0	27
Odor Objection Concentration (OOC) Based on Objection/Complaint	4.0	27

The OTC is limited in its ability to predict how consumers assess odors in their tap water. The OTC is determined in a controlled environment with no masking odors like chlorine present in the water. The panelists were striving under laboratory conditions to detect odor differences between three cups at eight concentration levels. That situation is far different than taking a glass of water from a kitchen faucet.

The ORC level determined in this study is higher than the OTC by a factor of 15. This finding is not inconsistent with limited peer-reviewed literature comparing detection and recognition thresholds.¹⁸ Both OOC levels are 27 times higher than the expert panel's OTC. Peer-reviewed literature does not provide much guidance on how high or low factors like this should be.

The OOC levels of 4.0 ppb are better values to use to gauge human response than the OTC. For example, setting a secondary standard for Crude MCHM would be best accomplished using estimates of the OOC, preferably with the results from a panel of untrained consumers. California did exactly this in 1999 when they set a 1 ppb secondary standard for Thiobencarb (a rice herbicide) that generated a bitter taste upon chlorination. Instead of using the expert panel findings, the California Department of Public Health used the level of complaints from consumers objecting to the taste of the water.¹⁹

The ORC is a better indicator than OTC for estimating the point where consumers recognize an odor. Many of the panelists described the odor of the water containing Crude MCHM below the individual ORC concentrations as sweet, which was not an odor that many objected to. The Louisville odor panel used a distinctive sweet odor to note the presence of MCHM in Ohio River water as the plume from the Elk River chemical spill passed their intake.²⁰

Minor components of the chemical compound mix called Crude MCHM could have an impact on the threshold concentrations experienced by panelists and consumers. We are still not certain that only the pure compound MCHM is responsible for the licorice odor in Charleston drinking water. More research is needed to determine the contribution of the minor components of Crude MCHM to the aesthetic responses experienced by Charleston residents.

It is not appropriate to look at only a portion of the responses by individual panelists in this study and extrapolate their determinations to the public at large. We have no idea if the individual responses of these nine expert panelists represent responses by any segment of the Charleston population. However the collective responses (with qualifiers) can give us guidance on consumer responses.

The most important finding of this work can be stated succinctly. The estimated thresholds determined in the Expert Panel study support consumer observations in Charleston, WV that people recognized and objected to the licorice odor caused by Crude MCHM in their drinking water even though the analytical reports were showing non-detect at a minimum reporting level of 10 ppb.

The only appropriate use of the results of this work is to cite the geometric means of the data generated by the panelists, which resulted in estimates of the OTC, ORC and OOC concentrations. The fact that these composite numbers reflect the general experience of the consumers exposed to Crude MCHM contaminated tap water strengthens the appropriateness of this conclusion.

Using the methodologies developed in this study, a group of untrained consumers should estimate the levels of OTC, ORC and OOC for Crude MCHM in water. We need to understand if the geometric mean values produced by the Expert Panel are significantly different from a group of untrained consumers.

Not surprisingly, many people in Charleston did not use tap water even after the “Do Not Use” restriction was lifted. They also did not start using tap water after they were told that the concentration of MCHM was non-detect. They continued not using tap water because their sense of smell recognized it and objected to its presence. For many people, smelling an off-odor in tap water means that it is not safe for them to drink.²¹

SUMMARY AND CONCLUSIONS

Based on the assessments in this report, the following points can be concluded:

1. A methodology was developed based on ASTM Method E679 to estimate the OTC, ORC and OOC concentrations for Crude MCHM in water during a single panel session.
2. Spiked concentrations of Crude MCHM were measured by a sensitive analytical method and found to be within acceptable percent recoveries.
3. The estimate of the Odor Threshold (Detection) Concentration for Crude MCHM in water determined by the Expert Panel was less than 0.15 ppb.
4. The estimate of the Odor Recognition Concentration for Crude MCHM in water determined by the Expert Panel was 2.2 ppb.
5. The estimates of the Odor Objection Concentration for Crude MCHM in water determined by the Expert Panel were found to be 4.0 and 4.0 ppb when measured using the Degree of Liking and Objection/Complaint methods, respectively.
6. The estimated thresholds determined in the Expert Panel study support consumer observations in Charleston, WV that people could recognize and object to the licorice odor caused by Crude MCHM in their drinking water even though the analytical reports were showing non-detect at a minimum reporting level of 10 ppb.

RECOMMENDATIONS

As a result of the findings from this study, the following actions are recommended:

1. Convene a large panel comprised of untrained consumers and determine the OTC, ORC and OOC concentrations using the same methodology used in the Expert Panel Study.
2. Change the range of concentrations presented to the consumer panel to 0.027 to 60 ppb using eight concentration levels separated by a factor (step) of 3. This range will hopefully capture the correct OTC, ORC and OOC responses by the individual consumer panelists.
3. Conduct oxidation studies of Crude MCHM with chlorine and potassium permanganate and determine if the odor characteristic or intensity of the licorice odor is changed after oxidation.

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Appendices

Appendix A

Procedure for Expert Panel

Panelists check in. After they complete checkin, they are directed to another room. In that room, a person will hand them a cup of water and ask them to sniff it. After the panelist sniffs the example odor in the cup, the staff person will say, ***“The odors in the water samples may contain substances that smell like what is in this bottle. Please describe in your own words what you think this smells like.”*** The panelist’s response is marked on a score sheet by the staff person.

The panelist is then directed to the consumer panel testing room. Once all of the panelists are seated, the panel session begins and the script is read.

Script for Expert Panel

All people are seated. In front of each person is:

1. Coding sheet
2. Pen (not a pencil)
3. Degree of Liking Scale
4. Cup of plain water (color of cup is different from the others)

Good evening. Thank you all for helping us out. Tonight we will be testing a compound that is sometimes found in drinking water. At very low concentrations some people find the aroma of the compound quite pleasant. At higher concentrations other people find it not so pleasant. Some people find nothing wrong with odor of the compound at all. We are trying to figure out how a large group of people in a controlled environment react to the odor of this compound.

We will present three cups of water to each of you 8 different times. For each cup, pick up the watch glass and cup just like this, swirl it gently and sniff the air above the water. Replace the watch glass. For each set of 3 cups, choose the cup that is different from the other two. Even if it is difficult for you to detect a difference in the three cups, you must select one cup that is different. If you want, you can re-sniff the cups. Circle the code on your score sheet representing the cup that is different. **Leader demonstrates.**

After you choose the cup that is different, write down the **Odor Description** representing the water in the different cup on the score sheet. Describe the smell of the water in your own words. If you smell the example odor that we presented to you in the other room, use that descriptor in the Odor Description blank. Next, write what the water smells like in the Odor Description Box. If the water in the cup smells like nothing, you can write ***“nothing.”***

Next, we want you to tell us how much you **like or dislike** the water with the odor in the cup that was different. Use the Degree of Liking Scale at your place.

Finally, some of the odors we are presenting to you may be objectionable. If the odor is **objectionable** and you would complain to your water utility or the bottled water company about it, please mark “Yes” in the Object/Complain column.

Please remember that there are no “wrong” answers here. We are trying to understand how you perceive the water samples.

The plain water is available for you to use at any time during the panel session.

Let’s begin with the first set of three cups. (Three cups are delivered to each panelist.)

Are there any questions?

Leader walks around the room answering questions and making sure that everyone is filling in the coding sheets as the session continues.

After finishing the 8th and last set of three cups, all the panelists stay in their seats. The leader collects the coding sheets and makes sure that they are all filled out. Then all the panelists can leave.

Appendix B

Score Sheet for Panelist Number _____

Sample Cup Codes			Office Use	Odor Description	Degree of Liking	Object/Complain? Y or N
473	475	088				
298	332	649				
030	275	900				
874	503	301				
263	253	451				
547	152	636				
063	195	140				
827	841	607				

Date: _____

Start Time: _____

Instructions:

1. Circle the number of the sample cup that has a ***different*** odor from the other two cups.
2. Describe the odor in the cup that is different. Use your own words. If the odor is like the odor in the sample you smelled before the panel, use that descriptor.
3. Record how much you like or dislike the odor in the different cup using the Degree of Liking Scale provided.
4. Do you object to the odor in the different cup? Would you call your water utility or bottled water company to complain about the odor in the different cup?

Appendix C

Degree of Liking Scale

1. I would be very happy to accept this water as my everyday drinking water.
2. I would be happy to accept this water as my everyday drinking water.
3. I am sure that I could accept this water as my everyday drinking water.
4. I could accept this water as my everyday drinking water.
5. Maybe I could accept this water as my everyday drinking water.
6. I don't think that I could accept this water as my everyday drinking water.
7. I could not accept this water as my everyday drinking water.
8. I could never drink this water.
9. I can't stand this water in my mouth and I could never drink it.